DTU Library

Extensional rheometer based on viscoelastic catastrophes outline.

Jensen, Kristian Ejlebjerg; Okkels, Fridolin; Szabo, Peter

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 December 2014 (31.12.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/206421 A1

(51) International Patent Classification:
G01N 11/00 (2006.01) ***G01N 11/02*** (2006.01)
B01L 3/00 (2006.01) ***G01N 11/08*** (2006.01)

(21) International Application Number: PCT/DK2014/050245

(22) International Filing Date: 15 August 2014 (15.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13180552.5 15 August 2013 (15.08.2013) EP
14159959.7 14 March 2014 (14.03.2014) EP

(71) Applicant: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelundsvej 1, Bygning 101A, DK-2800 Lyngby (DK).

(72) Inventors: **JENSEN, Kristian Ejlebjerg**; Rævehøjvej 36, room 506, DK-2800 Kgs. Lyngby (DK). **OKKELS, Fridolin**; Halfdansgade 33, 2. floor, DK-2300 Copenhagen S (DK). **SZABO, Peter**; Ravnsnæsvej 228, DK-2970 Hørsholm (DK).

(74) Agent: **PLOUGMANN & VINGTOFT A/S**; Rued Langgaards Vej 8, DK-2300 Copenhagen S (DK).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

— *upon request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a)*

(54) Title: EXTENSIONAL RHEOMETER BASED ON VISCOELASTIC CATASTROPHES OUTLINE

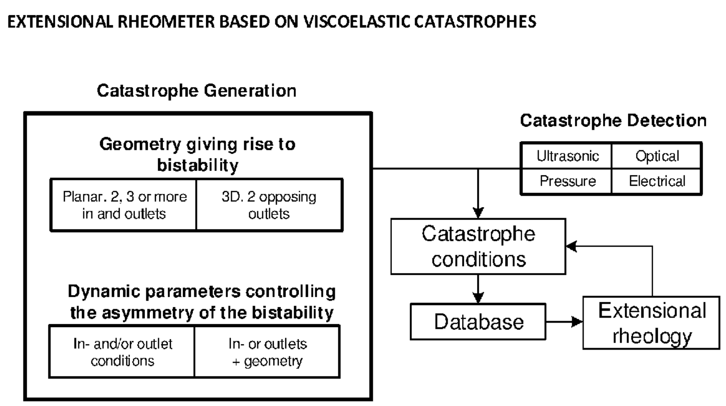


Fig. 7

(57) Abstract: The present invention relates to a method and a device for determining viscoelastic properties of a fluid. The invention resides inter alia in the generation of viscoelastic catastrophes in confined systems for use in the context of extensional rheology. The viscoelastic catastrophe is according to the invention generated in a bistable fluid system, and the flow conditions for which the catastrophe occurs can be used as a fingerprint of the fluid's viscoelastic properties in extensional flow.

WO 2014/206421 A1

EXTENSIONAL RHEOMETER BASED ON VISCOELASTIC CATASTROPHES

OUTLINE

FIELD OF THE INVENTION

The present invention relates to a method and a device for determining viscoelastic properties of a fluid. The invention resides inter alia in the generation of viscoelastic catastrophes in confined systems for use in the context of extensional rheology. The viscoelastic catastrophe is according to the invention generated in a bistable fluid system, and the flow conditions for which the catastrophe occurs can be used as a fingerprint of the fluid's viscoeleastic properties in extensional flow. It is noted that according to the knowledge of the inventors, viscoelastic catastrophes have not been reported in the scientific literature.

BACKGROUND AND OBJECT OF THE INVENTION

The viscoelastic properties of a fluid has been found to be of importance in production processes e.g. during production of plastic products. This, essentially, always involves extensional flow, which can cause instabilities that limit the quality and/or production rate. In particular, viscoelastic instabilities are undesired in polymer processing as they result in weaker products.

Today, determination of viscoelastic properties is often carried out by use of devices adapted to determine either shear or extensional rheology, the concept of a relaxation time is related to the later. While these methods are applicable to determine the properties, they are incompatible with automated process monitoring and are not scalable. This means that they require a significant minimum amount of liquid and that they cannot measure small relaxation times due to the presence of inertial effects on the macro scale.

Groismann, A et al (microfluidic memory and control devices; Science, American Association for the Advancement of Sience, Washington, DC; US, Vol. 300, 9 May 2003, pages 955-958) discloses a microfluid memory and control devices. Groismann, A et al discloses microfluidic fluidic control and memory elements through the use of an aqueous viscoelastic polymer solution as a working fluid, and demonstrate that by exploiting the fluid's non-Newtonian rheological properties a bistable flip-flop memory can be established. The bistable flip-flop memory is embodied as a "cross-road" where liquid is fed from two inlets and from where it is evacuated to the outlets. The two channels leading to the outlets are identical whereas the feeding channels have distinct geometries.

Groismann, A et al report two bistable flow states occurring at the same pressure at the inlets and outlets, and that a transition between the two states can occur when a sufficiently large perturbation is applied; an example of such a perturbation is reported as briefly blocking one of the outlets. The transition time between the two metastable states is reported to around 100 ms. It is noted that Groismann, A et al, refers to the two states as metastable; however according to the definitions used herein, the two states are considered to be bistable.

The purpose of the work reported by Groismann, A et al is to design a fluidic memory, that is a device mimicking an electronic digital circuit having two logical states "1" and "0". Although the properties of fluid used may be relevant in the working principle of the work reported by Groismann, A et al, the work focused on a *repeatedly*, fast and reliable shift between two bistable flow states.

Without being bound by theory, , it is highly questionably whether the flip-flop mechanism reported by Groismann, A et al mechanism can be used to characterise a fluid such as used to determine one or more fluid properties. This may inter alia be argued in the following manner: as the flip-flop mechanism resides in applying to the system a *perturbation* during a relatively small time scale (described as "by briefly blocking one of the outlets"), there seems to be only limited information extractable about the fluid from the system and/or the perturbation. This is due to the fact that the transition is imposed, and the time at which it occurs is thus independent of the fluid properties. Further, the flows through the inlets has each the same momentum before and after the perturbation whereby information as to the fluidic properties hardly – if not impossible – can be derived based on external controllable and detactable measures (such as volume flow). One could use the point of bistability in Groismann, A et. al.'s system as a fluid fingerprint, but it is very difficult to estimatate this point accurately due to the continuous nature of the transition. It is one of difficulties that the present invention addresses by associating the point of bistability with a spontaneous jump in the fluid flow.

Hence, an improved method and device for determining the properties of a viscoelastic fluid would be advantageous, and in particular a more efficient and/or reliable method and device for that purpose would be advantageous.

It is a further object of the present invention to provide an alternative to the prior art. In particular, it may be seen as an object of the present invention to provide a method and a device that solves the above mentioned problems of the prior art with respect to:

- Offline characterization incompatible with automated process monitoring
- Not down scalable entailing
    - Large minimum relaxation time due to inertial effects at macroscale
    - Large sample volumes

SUMMARY OF THE INVENTION

Thus, the above described objects are intended to be obtained in a first aspect of the invention by providing a method for characterizing a viscoelastic fluid. Often the characterization relates to determining the viscoelastic properties of a fluid.

The invention resides inter alia in the identification of the flow conditions (that is often the volume flow going into a fluid device), at which a so-called viscoelastic catastrophe occurs, as these conditions can be used as a fingerprint of the fluid's viscoelastic properties in extensional flow. That is, there exists a correlation between the flow conditions at which the viscoelastic catastrophe occurs and the viscoelastic properties. Thus, based on analyzing a number of viscoelastic fluids with known properties e.g. a database can be build, which contains corresponding values of flow conditions at which a viscoelastic catastrophe occurs and the properties of interest. This database may then provide the properties of interest of an unknown fluid, e.g. a fluid having unknown properties, when the flow conditions at which the viscoelastic catastrophe occurs have been determined. If a perfect match is not found, interpolation and/or extrapolation can advantageously be used.

The method utilizes a fluid device in the form of *a planar fluid device* having at least two inlet channels and at least two outlet channels arranged alternatingly (see e.g. fig. 1 and 5), or *a three-dimensional fluid device* having three or more inlet channels and two outlet channels pointing in opposite directions (see e.g. fig. 6). According to a broad aspect of the invention, the method comprises that the geometry and/or the flow conditions are modified such that the two bistable flow patterns are not a mirror of each other. The flow patterns in the fluid device are asymmetric, as will be disclosed in further details herein. The asymmetry constitutes a novelty compared to the fully symmetric patterns studied experimentally as well as theoretically in the academic literature.

On an overall level, the method according to the present invention comprises a number of steps occurring in the following consecutive order:

- feeding a viscoelastic fluid through the inlet channels of the fluid device,
- increasing the characteristic extension rate in the fluid device, such as by increasing total volume flow through the fluid device,
- varying the relative ratios of inlet flow rates or changing the geometry of the fluid device dynamically, typically and preferably at a timescale at least 10 times larger than the best estimate of the fluid's relaxation time
- decreasing the characteristic extension rate in the fluid device, such as by decreasing the total volume flow through the fluid device
- detecting the occurrence of a viscoelastic catastrophe
- recording the flow conditions at which a viscoelastic catastrophe occurs,
- determining the viscoelastic properties of the fluid based on the recorded flow condition.

In preferred embodiments, the method includes the feature of "increasing the total volume flow through the inflow channels (Q_1+Q_2) to a preselected total volume flow". The "preselected total volume flow" is often selected on an experimental and/or theoretical basis with the aim of obtaining the metastable flow condition during the method.

The present invention resides inter alia in that at high Weisenberg numbers, and when the flow has "selected" one of two asymmetric possible flow configurations in the fluid device, the flow is altered from the outside (as seen from the flow in the fluid device) in such a manner that one of the asymmetric flow configuration becomes metastable. This alteration is done purposely and thereby not as a result of an uncontrolled flow situation. The metastable flow configuration can be maintained stable as long time it is required, until the Weisenberg number is decreased to force the flow towards the viscoelastic catastrophe after which the system is no longer metastable.

When the Weisenberg number then is decreased, this can be done during a time period being arbitrarily slow; however, due to practical limitations, the time scale at which the Weisenber number is decreased is typically selected to be from ten times the Viscoelastic relaxation time (VERT) and upwardly.

According to the invention, the Weisenberg number is changed by changing the volume flow through the fluid device, and a characteristic of the method according to the present invention is that the viscoelastic catastrophe occurs at inflow conditions being different from inflow conditions at the onset of the method.

Compared to the work of e.g. Groismann, A et al, the present invention resides in that the two equally stable, bistable flow states produced by Groismann is not repeated by the present invention. In addition, according to the work of Groismann, A et al, one of the outlets are temporarely blocked – or a tremendous pressure is imposed – which at least temporarily corresponds to a change in geometry to a system having a single outlet only.

In the present invention, two asymmetric flow configurations are indeed possible but they are not equally stable; in fact, due to the asymmetries at in- and outlets, one of the asymmetric flow configurations is strengthened. This has the important effect that irrespectively of the time during which the total volume flow (Q_1+Q_2) is decreased with changing the asymmetry (Q_1/Q_2), the flow configuration will shift abruptly to another asymmetric flow situation. Hereby a spontaneous and recordable flipping can be obtained in a systematic way so as to extract information about properties of the fluid.

In certain preferred embodiments, the rate at which the increase and decrease in volume flow / extension rate occurs is in the region of ten times the viscoelastic relaxations time of the fluid. Often, such a time scale is not know a priori and in such cases, an indication on the time scale may be found in tables on similar fluids. If no information is available, a value of seconds can be used as an initial guess and the method may be repeated with constantly smaller values of VERT until viscoelastic catastrophes start to occur.

It is noted that, although the imposed changes modifies the asymmetry of the flow patterns, two bistable flow possibilities continue to exist (until the catastrophe occurs) although only one of them is present in the flow.

LIST OF TERMS

In the present context, a number of terms have been used in a manner being ordinary to a skilled person. However, some of these terms are elaborated below:

Bistable flow is preferably used to mean that there exists two (or more) possible flow configurations for the same in- and outlet conditions, see right insets of fig. 2a (showing stream lines), where the symmetric case is illustrated. This is special in the sense, that the device will pick a flow configuration at random, when the volume flow is turned up.

Best estimate of a fluid's relaxtion time is preferably used to mean an initial guess supplied by the operator of the method/device; if left clueless, 5 seconds is taken as a default value.

Asymmetric bistability is preferably to be understood in the context of fig. 2b. It is preferably used to mean that the flow is bistable, but that only one of the flow configurations is connected to the solution at slow volume flow. That is, the device will pick the same flow configuration every time the volume flow is turned up.

Bistable regime is preferably to be understood in the context of fig. 2. It means that the volume flow is sufficiently fast for the flow to be bistable. Volume flows below a critical value give rise to a single stable flow configuration.

Asymmetry is preferably used to characterise a feature having no rotational or mirror symmetry. This can be due to the geometry as well as certain conditions at in- and outlets.

Asymmetric flow (or asymmetry of the flow pattern) is preferably used to mean that the streak or stream lines of the fluid are asymmetrical.

Fluid is preferably used to mean a liquid, gas, plasma and/or combinations thereof. The fluid may further contain solid matter, typically in the form of particles.

Ground state is to be understood in the context of asymmetric bistability. It is preferably used to mean the flow configuration associated with the least hydraulic resistance and connected to configuration at low flow rates (when the system is not bistable). For pressure driven systems this corresponds to the flow configuration associated with the highest dissipation, while it corresponds to the lowest dissipation for flow driven systems.

Metastable flow is to be understood in the context of asymmetric bistability. It is the flow solution that is not the *ground state*.

Flipping asymmetry of the bistability is preferably used to mean that the connectivity of the flow configuration is changed such that the flow configuration, that used to be chosen every time the volume flow is turned up, is no longer chosen. Instead it is the other asymmetric flow that is chosen (see fig. 3a-b), i.e. the system is set in a metastable state.

Viscoelastic relaxation time (VERT) of a fluid is preferably used in a manner being ordinary to a skilled person. In many preferred embodiments of the invention, the actual value of VERT may be unknown (as the fluid in question in unknown) and in such situations, a number of tests are performed prior to executing the steps according to the present invention in order to determine the value of VERT. "Viscoelastic relaxation time" and "relaxation time" are used interchangeably herein.

Viscoelastic Catastrophe is preferably used to mean that the flow shifts from a metastable configuration to the ground state, because the metastable configuration ceases to exists. The shift occurs abruptly, typically in the sense that the time during which the shift in asymmetry occurs within a timescale in the order of the viscoelastic relaxation time,λ ,of the fluid. Typically, the relaxation time is $\lambda < 10$ ms, such as $\lambda < 8$ ms, such as $\lambda < 6$ ms, such as $\lambda < 5$ ms, such as $\lambda< 4$ ms and even $\lambda< 3$ ms. It is noted, that the relaxation time and is correlated with the shear rate, γ, by the Weissenber number $We=\lambda*\gamma$ (whith the dimension λ [seconds] and γ [1/seconds]). Typically and preferably, $We > 0.5$ during use of the present invention which may be used to dimension (flow as well as geometric parameters) specific embodiments according to the present invention.

Rheometer is preferably used to mean a device suitable for determining viscoelastic properties of a viscoelastic fluid. In the present context, the fluid device forms part of the rheometer which also includes a system for detecting the viscoelastic catastrophe as well as any necessary motors, pumps, valves or taps for generating the flow conditions that cause the viscoelastic catastrophe.

Characteristic extension rate – or extension rate - is preferably used in a manner being ordinary to the skilled person. A change in characteristic extension rate may typically accomplished by changing the volume flow through the device.

In many preferred embodiments, the method is carried out by use of a planar fluid device. Such a device will, of course, have a 3-dimensional extension, but is considered to be a planar fluid device as the fluid flow can be described with two coordinate directions (e.g. x, y) and does not contain a substantial flow normal to these two coordinate directions.

In other preferred embodiments, the method is carried out by use of a three-dimensional fluid device. Such a device has a 3-dimensional extension and the fluid flows in three coordinate directions (e.g. x, y, z).

In some embodiment, the geometry of the fluid device is changeable. This is used to e.g. introduce asymmetry or to flip the asymmetry of the bistability. The changeable geometry of the fluid device may include flexible walls in general and walls which are arranged in the fluid device in a manner where their relative position in the fluid device may be changed.

Further aspects and embodiments are presented in the following as well as in the accompanying claims.

The various aspects of the invention are disclosed herein may each be combined with any of the other aspects. These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter and in the accompanying claims.

BRIEF DESCRIPTION OF THE FIGURES

The present invention and in particular preferred embodiments thereof will now be described in more detail with regard to the accompanying figures. The figures show ways of implementing the present invention and are not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 discloses schematically a cross-slot geometry of a rheometer according to the present invention, upper part of figure 1 shows the cross-slot in perspective and the lower part of the figure 1 shows a horizontal cross sectional view of the cross-slot,

Figure 2 discloses schematically a pitchfork bifurcation produced according to the invention. Both symmetric (a) and asymmetric bistability (b) is illustrated. The inserts showing stream lines in (b) are for guidance only, as they will in general not be a mirror of the ones in (a),

Figure 3 discloses schematically various states of fluid flow and how they are produced during determination of the viscoelastic properties, the Q_1 and Q_2 being inlet flow rates in an example of how the viscoelastic catastrophe can be generated.

Figure 4 is a flow-chart of a method according to the invention,

Figure 5 discloses schematically a planar fluid device having three inlets (symbolic referenced by arrows indicating inflow) and three outlets arranged alternatingly,

Figure 6 discloses schematically a 3-dimensional fluid device having four inlets (symbolic referenced by arrows indicating inflow) and two outlets, and

Figure 7 is an overall illustration of the invention.

DETAILED DESCRIPTION OF AN EMBODIMENT

Reference is made to fig. 1 which discloses schematically a cross-slot 1 of a rheometer according to the present invention. In fig. 1a, the cross-slot 1 is shown in perspective and in fig. 1b, a horizontal cross sectional view is presented. The cross-slot of fig. 1 is an example of a planar fluid device having at least two inlet channels and at least two outlet channels alternatingly arranged.

As illustrated in fig. 1, the cross-slot 1 has four openings 2 two of which are used as inlets and two of which are used as outlets. Internally, the cross-slot in fig. 1 forms a channel system with a stagnation region in the centre of the cross. The openings 2 are typically identically shaped and operates as inlet or outlets based on the way the fluid is fed into and leaves the cross-slot 1. It is noted that although the cross-slot is shown having channels with constant a rectangular cross section, these channels may have other cross sections, such as circular cross sections, as well as have changing cross-sections, such that fluid flows through contractions or expansions. As indicated in fig. 1, fluid is flowing into cross-slot 1 with flow rates Q_1 and Q_2.

The fluid is fed into the cross-slot through at least two opposing openings 2 so that the two fluid stream flow towards each other, preferably antiparallel to each other.

The flow inside the cross-slot at a given time instant depends inter alia on the history, i.e. how the fluid has been fed into the cross-slot 1 at previous time instants as well as the viscoelastic properties of the fluid. However, in total one part of the fluid will flow out through one of the outlets and the remaining fluid will flow out through the other outlet.

Inside the cross-slot 1, the flow will be characterised by that stream lines do not cross each other, and at least two flow configurations may exist for the same conditions at the in- and outlets. In other words, the system may be bistable:

I A symmetric flow situation where incoming fluid from one inlet is divided symmetrically to both the outlets – see fig. 2a, left hand insert (stream lines).

II A asymmetric flow situation where incoming fluid from one inlet flows mostly towards a single outlet – see fig. 2a, right hand inserts (stream lines).

The graphs of fig. 2 are what generally may be termed bifurcation diagrams. The vertical axis represents rotation of the flow, while the brighter and darker areas represent areas with increasing clock- and counterclockwise rotation, respectively. The inserts show the symmetric and two asymmetric solutions at their respective positions in the diagram.The horizontal axis represents values ranging from "slow flow" to "high flow" – examples on the absolute values of slow and high relates to the properties of the fluid as well as the volume flow and will be disclosed below.

Fig. 2a shows a pitchfork bifurcation. The "slow flow" is characterised by being symmetric and the flow remains so with increasing flow until the bifurcation point is reached. A further increase of the volume flow, results in two flow configurations with reduced symmetry (only rotational). The symmetric configuration still exists, but it has become unstable (dashed) and thus unphysical. Both configurations with reduced symmetry are connected to the solution at slow flow.

This is different when asymmetry is introduced, either in the geometry (the outlets being of different lengths as shown in fig. 1), the inlet(s)/outlet(s) and/or the conditions at the in- and outlets. Note, that there should preferably be an asymmetry between the two inlets as well as the between the two outlets in order for the asymmetry to be sufficiently broken to give a situation as illustrated in fig. 2b. The bifurcation changes into a situation as indicated in fig. 2b, where one of the stable flow configurations has become disconnected as indicated by the solid white line continuing into the unstable (dashed) solution rather than the other stable solution. Two asymmetric modifications can give rise to the bifurcation shown in (b), and it is possible to choose these modification such that one of them can be used to flip the asymmetry of the bistability. This enables the device to be set in the disconnected/metastable state as illustrated in fig. 3. Please note the numbers in fig. 3; they indicate the sequence the system is going through.

As it appears from fig. 3 four steps may be carried out in the following consecutive order:

1) #1->#2; the system is moved to the bistable region by increasing the total volume flow (the bifurcation parameter) while maintaining the ratio of Q_1/Q_2 constant, thereby one of the asymmetric states is selected,
2) #2->#3; the asymmetry of the bistability is flipped while maintaining the total volume flow (Q_1+Q_2); thereby the system is put in a metastable state
3) #3->#6; the general flow rate (total volume flow) is slowly decreased while maintaining the Q_1/Q_2 constant, which gives rise to an equivalent slow change in the flow until
4) #4->#5; the catastrophe occurs.

It is noted, that in fig. 3d, the process is shown as continued after point #5. However, although this is indeed possible, the present invention makes use of the flow conditions at point #4, that is typically the volume flows Q_1, Q_2 and/or the ratios of Q_1 and Q_2. It is noted, that the way to reach point #4 – e.g. as depicted in fig. 3d – may be considered of lesser relevance in connection with the present invention as long as the system is brought into a metastable flow situation. Accordingly, fig. 3e may be seen as a representing a typical alteration of flow conditions during a procedure leading to characterization of a fluid according to the present invention.

An alternative view of the asymmetric bistability is provided in fig. 3c, where the hydraulic resistance is plotted on the vertical axis. It illustrates that a measurement of this quantity – and many others - will show a sudden change when the catastrophe occurs.
This simplifies detection of the catastrophe as well as the particular critical flow rate, which is characteristic for the extensional rheology of the working fluid.

With reference to fig. 3a-d, the creation of a catastrophe according to the present invention will now be disclosed in greater details. As disclosed above, the present invention resides in that two asymmetries are imposed and in the example shown in fig. 3, these two asymmetries are (see fig. 1):

- $L_{out,up} \neq L_{out,down}$ (which is referred to as a first asymmetry)
- $Q_1 \neq Q_2$ (which is referred to as a second asymmetry)

It is noted, that while the first asymmetry is fixed by the geometry and therefore often remains fixed (unless a variable geometry device is used), the second asymmetry is related to the flow at the openings of the device, and such parameters are often changeable. Based on these two asymmetries, the method of characterising a fluid comprises the following consecutively performed steps:

i) Initially, the fluid is fed into the two inlets (#1) at first flow rates Q_1, Q_2 being different from each other which result in that the flow is onset in a state with a single stable flow configuration.

ii) Thereafter, the total volume flow Q_1+Q_2 is increased while the volume flow ratio Q_1/Q_2 is kept constant (see fig. 3d: #1->#2). In point #2 the system is in a bistable regime, but still in the ground state.

iii) After having reached point #2 in fig. 3, the total volume flow, Q_1+Q_2, is now kept constant, while the volume flow ratio, Q_1/Q_2, is slowly altered such that the flow rates Q_1 and Q_2 are interchanged, which has the effect of flipping the asymmetry of the bistability and thus also achieving a metastable state. Thereby, it is no longer possible to bring the fluid back to the state it had in point #2 and #1 by reversing step ii) above.

iv) The total volume flow, Q_1+Q_2, is now decreased, while the volume flow ratio, Q_1/Q_2, is kept constant. At some instant during the decrease of the total volume at constant volume flow ratio, the viscoelastic catastrophe will occur.

The method of creating the catastrophe and determining the instant where the catastrophe occurs are schematically shown in the flow diagram of fig. 4.

Reference is made to fig. 5 which discloses schematically a planar fluid device having three inlets and three outlet arranged alternatingly. Fig. 5 discloses the planar fluid device as a cross-sectional view and the 3-dimensional shape of the fluid device of fig. 5 is as the fluid device disclosed in fig. 1 but instead of having two inlets and two outlets, the device of fig. 5 has three of each. The inlet channels and outlet channels, are alternatingly arranged, that is in circumferentially direction an inlet flanked by two outlets (and an outlet is flanked by two inlets). Please note, that in fig. 5 only arrows referring to inflow mark the inlets; the outlet is not marked, but occurs through the remaining channels. Numerical experiments with the device of fig. 5 have shown that bistability can be produced, and that is it is possible to generalize the above outlined methodology for the cross-slot to this or other planar devices with even more in- and outlets.

When more than two inlets are used, the methods disclosed above with reference to two inlets is extrapolated to a set-up with more than two inlets. The extrapolation of the method to more than two inlets is considered within the reach of a skilled person and may be performed in number of different manners bearing in mind a common feature (for embodiments with two or more inlets) is that the flow is to be brought into a meta-stable flow configuration. Thus, fig. 3d and fig. 3e may be seen as projections on a two-dimensional space of the flow evolution in case of more the two flow paramaters (Q_1, Q_2).

Figure 6 discloses schematically a 3-dimensional fluid device having four inlets and two outlets. Without being bound by theory, it is found that the number of outlets may be important, since numerical experiments indicate that, that two outlets give rise to bistability.

An important point is the asymmetry on the outlet as well as on the inlet side, as the catastrophe cannot be generated with the symmetric designs described in the present academic literature.

The invention involves a technique for detecting the viscoelastic catastrophe. The nature of the viscoelastic catastrophe allows for many different detection techniques, since any signal related to the flow near the stagnation point will jump, when the visoelastic catastrophe occurs. Alternatively one might differentiate the signal with respect to time and observe the catastrophe as a peak. The following techniques may be used

- Optical birefringence for transparent fluids.
- Ultrasonic response.
- Impedance characterization for fluids with electrical properties.
- Pressure sensors.
- Temperature sensors at outlets in combination with selective heating of the inlets.

Fig. 7 shows on an overall level various preferred features of the invention. As presented, the invention preferably involves two overall concepts namely catastrophe generation and catastrophe detection. The generation of the catastrophe is typically accomplished based on geometry giving rise to bistability or control of a dynamic parameter; However, combinations between these two are considered within the reach of the present invention. As also indicated in fig. 7, the detection may be performed by various means (ultrasonic, optical, pressure, electrical, temperature) and the detection is used in combination with a database to perform extensional rheology. The present invention may advantageously be implemented in-line with a production line.

When a fluid with unknown properties is to be characterised, the determination of the viscoelastic properties is based on comparing the flow condition at which a viscoelastic catastrophe occurs for an unknown fluid with values of flow conditions at which a viscoelastic catastrophe occurs for known viscoelastic fluids. Such flow conditions and correlated viscoelastic properties are typically stored in a database.

It is considered rare, that a true match is found between flow conditions for a known fluid and for an unknown fluid and a determination according to the present invention may preferably comprise interpolating between those fluids which based on the comparison are found to come closest to the unknown fluid.

The present invention also relates to a rheometer comprising a fluid device in the form of

a planar fluid device having at least two inlet channels and at least two outlet channels alternatingly arranged (fig. 1, fig. 2), or

a three-dimensional fluid device having three or more inlet channels and two outlet channels pointing in opposite directions (fig. 6),

and being adapted to carry out the method as outlined herein.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

CLAIMS

1. A method for characterizing a viscoelastic fluid, the method utilizes a fluid device in the form of a planar fluid device having at least two inlet channels and at least two outlet channels alternatingly arranged, or a three-dimensional fluid device having three or more inlet channels and two outlet channels pointing in opposite directions,the method comprising the consecutive steps of:

- feeding the fluid into the inflow channels with different volume flows (Q_1,Q_2),
- increasing the total volume flow through the inflow channels (Q_1+Q_2) to a preselected total volume flow, while maintaining the ratio (Q_1/Q_2) between the different volume flows,
- recording the asymmetry of the flow pattern in a stagnation region of the fluid device,
- maintaining the total volume flow through the inflow channels (Q_1+Q_2), while changing the ratio (Q_1/Q_2) between the two volume flows, preferably by increasing the ratio (Q1/Q2) between the two volume flows, such that they become interchanged
- decreasing the total volume flow through the inflow channels (Q_1+Q_2) while maintaining the ratio (Q_1/Q_2) between the volume flows and recording the total volume flow at which the flow pattern changes abrubtly.

2. A method according to claim 1, wherein the step of maintaining the total volume flow through the inflow channels (Q_1+Q_2), while increasing the ratio (Q_1/Q_2) between the two volume flows, comprising changing the ratio (Q_1/Q_2) between the two volume flows such that the inflow rates (Q_1, Q_2) become interchanged.

3. A method according to claim 1 or 2, wherein the rate at which the volume flows are altered occurs on a time scale at least 10 times larger than the viscoelastic relaxations time of the fluid.

4. A method according to any of the preceding claims, wherein the volume flows are controlled by changing the pressure at the inlet(s) and/or outlet(s), preferably be selective heating of the inlet streams.

5. A method according to any of the preceding claims utilizing a planar fluid device comprising two inlet channels and two outlet channels wherein the inlet channels and outlet channels extend in opposite directions from a flow stagnation region.

6. A method according to any of the preceding claims, wherein the fluid device is asymmetric by two outflow channels being of different lengths or the pressure at the outlet openings being different.

7. A method according to the any of the preceding claims, wherein the detection of the abrubtly changing flow pattern (the viscoelastic catastrophe) is carried out by identifying an abrupt change in the optical or ultrasonic response of the flow.

8. A method according to any of the preceding claims 1-6, wherein the detection of the abrubtly changing flow pattern (the viscoelastic catastrophe) is carried out by identifying an abrupt change in the pressure field of the flow.

9. A method according to any of the preceding claims 1-6, wherein the detection of the abrubtly changing flow pattern (the viscoelastic catastrophe) is carried out by identifying an abrupt change in the electrical response of the flow.

10. A method according to any of the preceding claims 1-6, wherein the detection of the abrubtly changing flow pattern (the viscoelastic catastrophe) is carried out by identifying an abrupt change in the temperature of the fluid at an outlet.

11. A method according to any of the claims 7-10, wherein an abrupt change is considered to occur if a change occurs within a timescale in the order of the viscoelastic relaxation time of the fluid.

12. A method according to any of the preceding claims, wherein the determination of the viscoelastic properties is based on comparing the flow condition at which a viscoelastic catastrophe occurs for an unknown fluid with values of flow conditions at which a viscoelastic catastrophe occurs for known viscoelastic fluids.

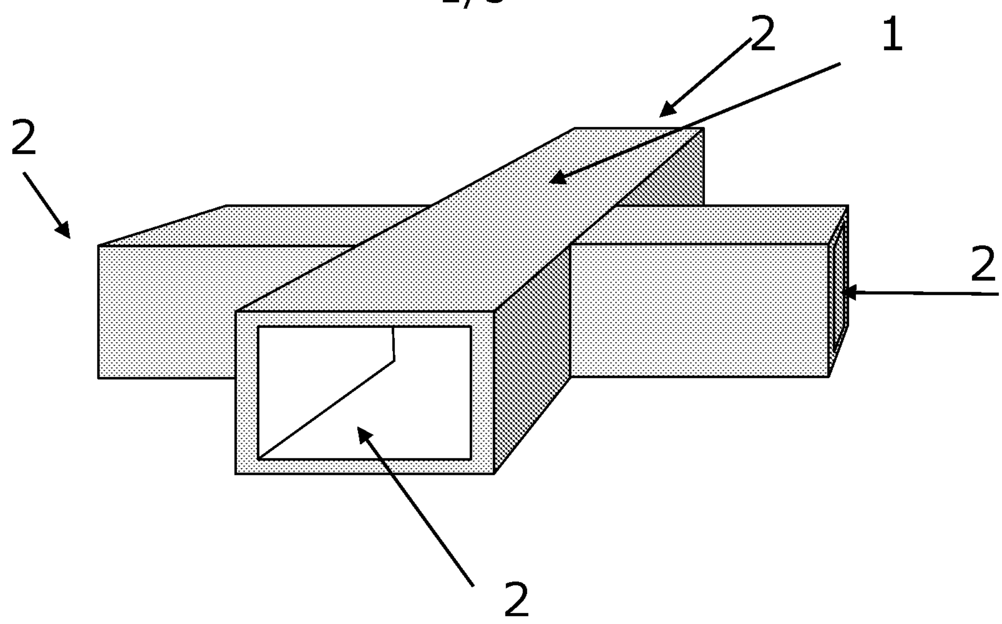
13. A method according to claim 12, wherein the determination comprising interpolating between those fluids which based on the comparison is found to come closest to the unknown fluid.

14. A method according to claims 12 or 13, wherein the flow conditions at which a viscoelastic catastrophe occurs for known viscoelastic fluids is stored in a database.

15. A rheometer comprising a fluid device in the form of

- a planar fluid device having at least two inlet channels and at least two outlet channels alternatingly arranged (fig. 1, fig. 2), or
- a three-dimensional fluid device having three or more inlet channels and two outlet channels pointing in opposite directions (fig. 6),

and being adapted to carry out the method according to any of the preceding claims.



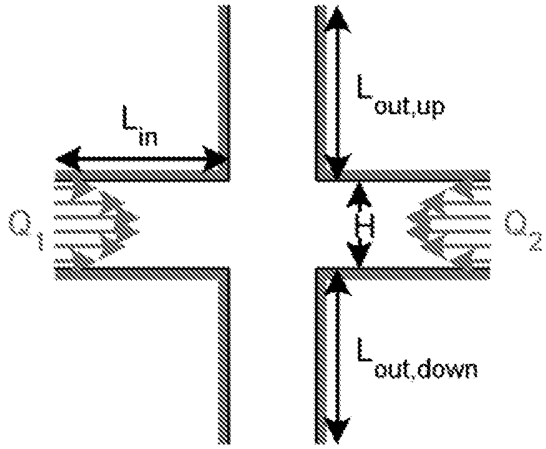
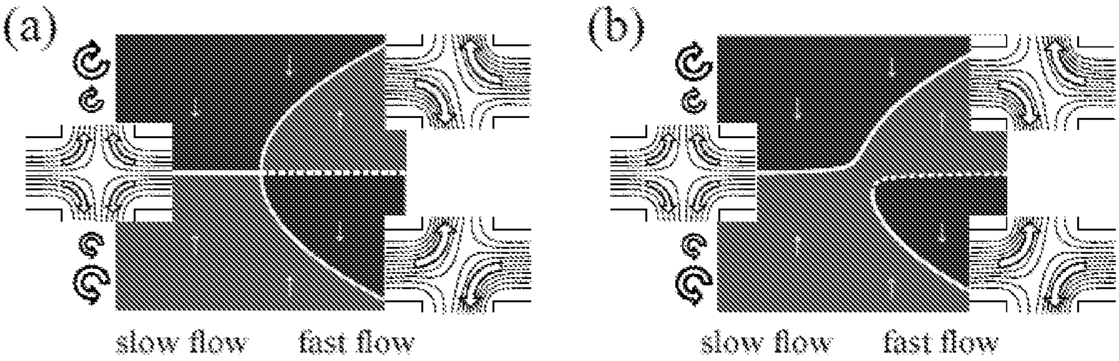
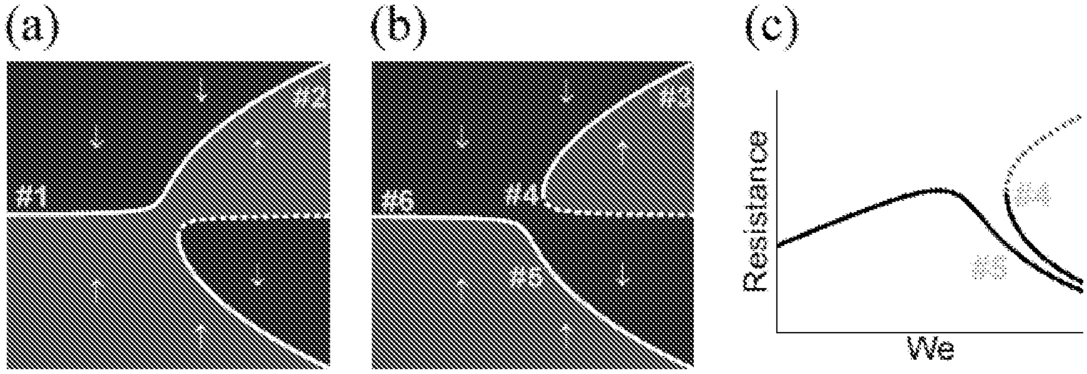


Fig. 1

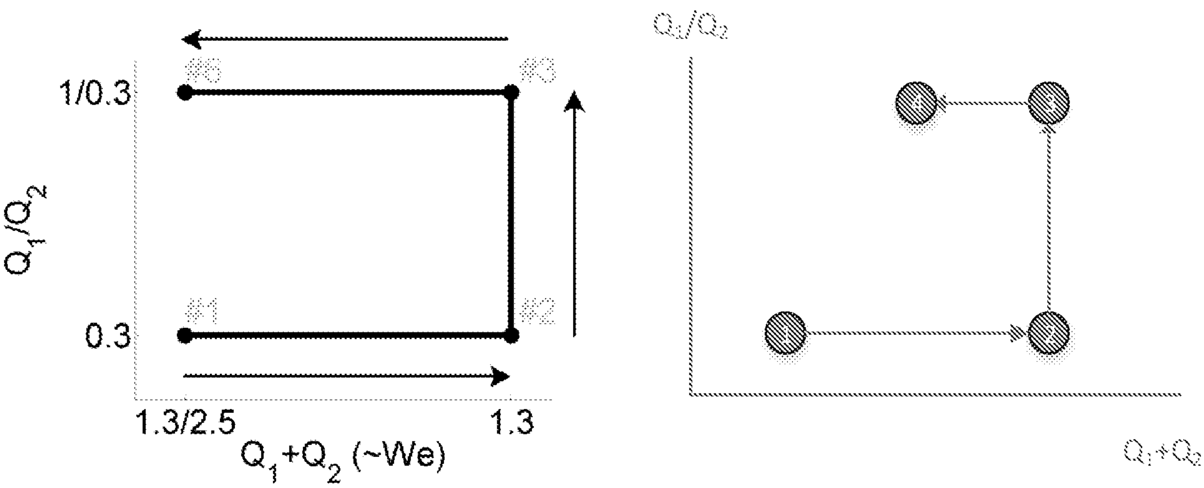


[redacted]



[redacted]

[redacted]



[redacted]

feed fluid into the inflow channels with two different volume flows (Q_1,Q_2) in opposite directions towards the flow stagnation region

increasing the total volume flow of the two different volume flows (Q_1,Q_2) to a preselected total volume flow, while maintaining the ratio (Q_2:Q_1) between the two different volume flows,

Record the asymmetry of the flow pattern in the stagnation region.

maintain the total volume flow of the two different volume flows (Q_1,Q_2), while increasing the ratio (Q_2/Q_1) between the two different volume flows,

decreasing the total volume flow while maintaining the ratio (Q_2:Q_1) between the two different volume flows and recording the total volume flow at which the asymmetry previously recorded in the stagnation region abruptly shifts into another asymmetric flow pattern in the stagnation region,

determining the characteristic of the fluid on the basis of the recorded total volume flow.

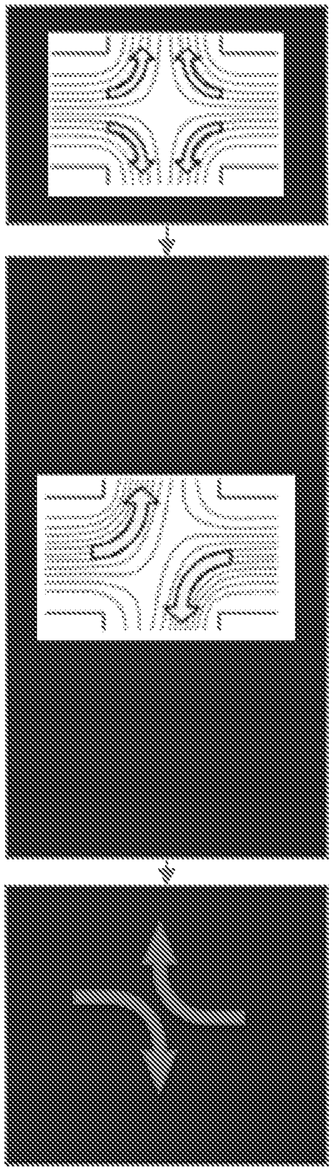


Fig. 4

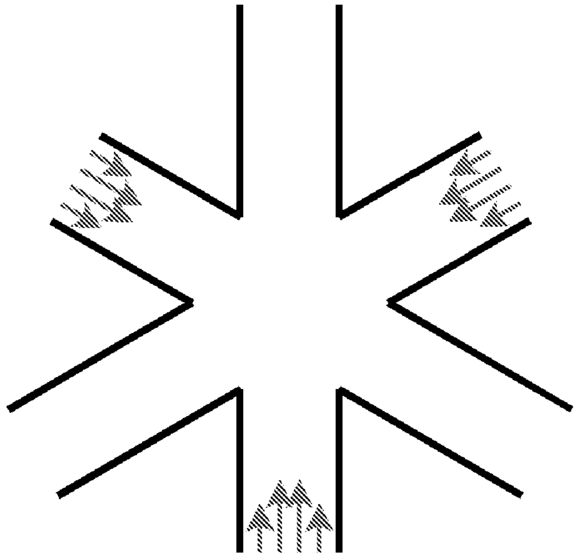


Fig. 5

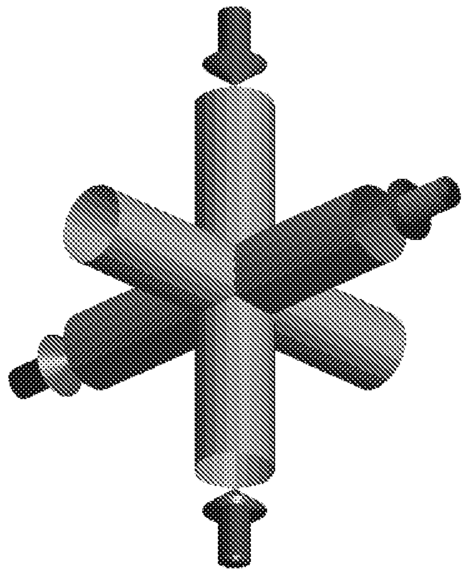


Fig. 6

EXTENSIONAL RHEOMETER BASED ON VISCOELASTIC CATASTROPHES

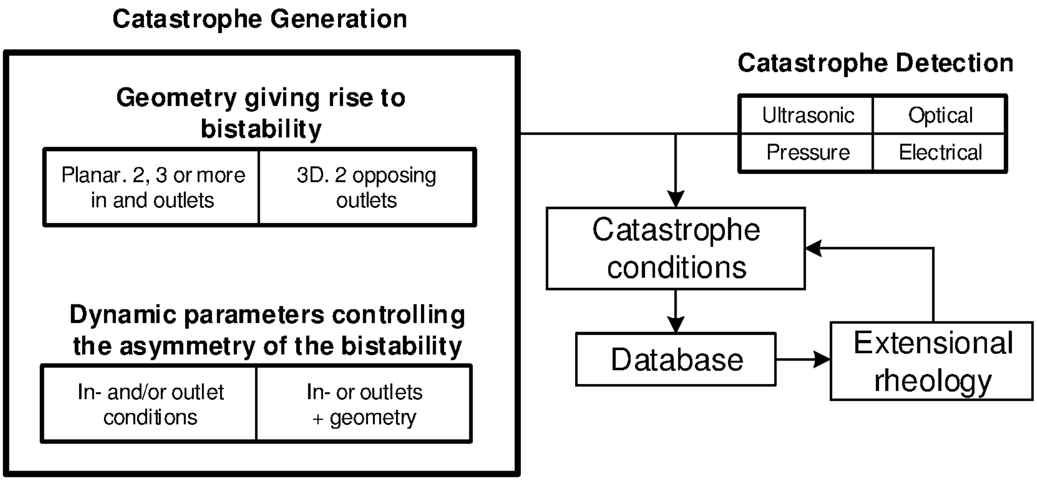


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2014/050245

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N11/00 B01L3/00 G01N11/02 G01N11/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N B01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KRISTIAN E JENSEN ET AL: "Optimization of Bistable Viscoelastic Systems", 10 TH WORLD CONGRESS ON STRUCTURAL AND MULTIDISCIPLINARY OPTIMIZATION, WCSMO10, ID5152, 19 May 2013 (2013-05-19), pages 1-10, XP055130829, Orlando, Florida, USA	1-3,5-15
Y	the whole document	4

-/--

[X] Further documents are listed in the continuation of Box C.

[ ] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 October 2014	30/10/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zarowna-Dabrowska, A

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GROISMAN A ET AL: "microfluidic memory and control devices", SCIENCE, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, US, vol. 300, 9 May 2003 (2003-05-09), pages 955-958, XP002409454, ISSN: 0036-8075, DOI: 10.1126/SCIENCE.1083694 the whole document -----	1-3,5-15
X	TODD SQUIRES ET AL: "Microfluidics: Fluid physics at the nanoliter scale", REVIEWS OF MODERN PHYSICS, vol. 77, no. 3, 6 October 2005 (2005-10-06), pages 977-1026, XP055088729, ISSN: 0034-6861, DOI: 10.1103/RevModPhys.77.977	1-3,5-15
Y	page 995 - page 1001; figure 28 -----	4
X	A.M. AFONSO ET AL: "Purely elastic instabilities in three-dimensional cross-slot geometries", JOURNAL OF NON-NEWTONIAN FLUID MECHANICS, vol. 165, no. 13-14, 1 July 2010 (2010-07-01), pages 743-751, XP055088577, ISSN: 0377-0257, DOI: 10.1016/j.jnnfm.2010.03.010	1,2,5, 12,15
A	the whole document -----	3,6-11, 13,14
A	P. E. ARRATIA ET AL: "Elastic Instabilities of Polymer Solutions in Cross-Channel Flow", PHYSICAL REVIEW LETTERS, vol. 96, no. 14, 14 April 2006 (2006-04-14), XP055089206, ISSN: 0031-9007, DOI: 10.1103/PhysRevLett.96.144502 the whole document -----	1-15
A	R. POOLE ET AL: "Purely Elastic Flow Asymmetries", PHYSICAL REVIEW LETTERS, vol. 99, no. 16, 18 October 2007 (2007-10-18), XP055089287, ISSN: 0031-9007, DOI: 10.1103/PhysRevLett.99.164503 the whole document -----	1-15

-/--

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ROBERT J POOLE ET AL: "PURELY-ELASTIC FLOW INSTABILITIES IN A MICROFLUIDIC CROSS-SLOT GEOMETRY", ALCHE ANNUAL MEETING, 4 November 2007 (2007-11-04), XP055131534, Salt Lake City, USA the whole document -----	1-15